

Testing DFT ability to predict the stereoselectivity of group 4 metallocenes in propylene polymerization

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ABSTRACT

In this study we have tested the ability of a standard DFT computational protocol to reproduce the experimentally obtained stereoselectivity of 26 different C_2 -symmetric zirconocene catalysts active in propylene polymerization. The catalysts were chosen for their relevance in metallocene catalyzed polymerization of propylene. To this end, primary insertion of both *si*- and *re*-propylene enantiofaces into the $Zr-CH_2-CH(CH_3)_2$ bond was considered to simulate the growing chains step. The energy difference between these two transition states, ΔE_{re-si} , was taken as a measure of the stereoselectivity (pentad: mmmm%) of different catalysts. The results clearly indicated that there was a good agreement between ΔE_{re-si} and the mmmm% values, so that greater ΔE_{re-si} could correspond to higher mmmm%. A model was fitted to the experimentally obtained mmmm% against theoretical ΔE_{re-si} . The coefficient of determination (R^2) of the resultant plot was 0.9793, which indicated a good accuracy of the model. Finally, to quantify the steric role of the studied ligands in the observed stereoselectivity, the analysis of the buried volume (V_{Bur}) and of the steric maps was performed for two representative complexes. The images revealed that a greater asymmetric localization of the % V_{Bur} around the metal center led to a higher mmmm% in the resultant polymer. **Polyolefins J (2014) 1: 139-146**

Keywords: Metallocene catalysts, DFT, Molecular simulation, Stereoselective polymerization, Isotactic polypropylene.

INTRODUCTION

Metallocene-based complexes are a remarkably relevant family of olefin polymerization catalysts [1]. In this context, the first attempts to use metallocenes as catalysts with defined structure were due to Breslow, Newburg [2] and Natta [3] that showed that titanocene in combination with aluminum alkyl halides could be used as homogeneous catalyst system to polymerize ethylene. However, its industrial application was not directly possible due to low activities.

The discovery of methylaluminoxane (MAO) as

cocatalyst by Sinn and Kaminsky in 1980 marked the most significant turning point in the field of metallocene catalysis [4]. The activity of the metallocene dichloride complexes of titanium, zirconium and hafnium was increased by orders of magnitude, thanks to the use of this new cocatalyst. Despite the good rise of activity for metallocene catalysts, thanks to the easy affordability of suitable organometallic cocatalysts, the development of stereoselective metallocene-based catalysts has demanded more effort due to the required development of chiral and stereorigid systems.

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In this regard, *ansa*-metallocenes bearing the two cyclopentadienyl ligands bound to the metal, and linked by a bridging group, have been thoroughly investigated during the past decades for stereoselective α -olefins polymerization [5-7]. In fact, the link prevents the rotation of the cyclopentadienyl ligands making these systems potentially suitable for a greater control of the stereochemistry at the metal centre [8-9].

Theoretical chemists have contributed much to shed light on the mechanistic behavior of these catalysts, taking also the advantage of the well-defined chemical structure of homogeneous metallocenes catalysts [10-11]. The elementary steps and the stereocontrol mechanism of olefin polymerization by groups 3 and 4 metallocenes have been a matter of intense mechanistic study since the beginning. Indeed, stereoselectivity and also regioselectivity of propene polymerization by metallocenes [12-15], non-metallocenes [16-18], heterogeneous Ziegler-Natta systems [19-24], as well as of styrene polymerization by half-metallocenes [25], have been rationalized by theoretical methods. These successful applications of computational methods suggest that they can be used for catalyst design to optimize the existing catalysts or to achieve the route towards new catalysts. However, we believe that a systematic validation of computational protocols should be performed, in order to assess the reliability of theoretical prediction to outline the systems to be further investigated experimentally [26]. With this aim, we test here a standard and computationally convenient protocol to reproduce the experimental stereoselectivity of 26 different metallocene systems active in propene polymerization.

Judging from the more recent literature, there is a quite good consensus that, for propene polymerization, the insertion barrier is usually rate-limiting even for efficient catalysts, making computational studies allowed to concentrate on this step to investigate the selectivity of the reaction. As a consequence, we focus here on the energetics of propene insertion into the M-alkyl bond. Zirconium has been selected as metal and, consistent with literature, the generic chain growth step is modelled through insertion into a Zr-isobutyl bond (Chart 1).

The choice of metallocene-made polypropene as the subject of this work comes from the evidence that, although 45 years old, the catalytic polymerization of propene is still evolving and growing both for higher production and for the wide range of applications

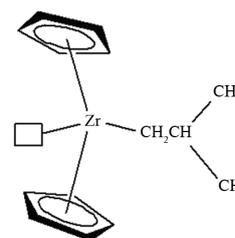


Chart 1.

and metallocene catalysts cover a large slice of PP production.

As a final remark, we note that a thorough comparison should be based on free energy data, rather than potential energy values and we restricted the analysis to potential energy values for two main reasons. First, extensive screening requires fast computational methods, and thus eliminating the frequency expensive computational calculation step reduces the overall computational cost remarkably. Second, the two transition states we compared only differ in the relative orientation of the growing chain and the methyl group of propene, and thus it is reasonable to expect that entropy differences would be minor. Indeed, several previous papers have indicated that the simple potential energy, even based on empirical force fields, already captures rather well the relative stereoselectivity of these systems.

Computational details

Density functional theory "DFT" calculations were performed with the Gaussian 03 package [27] using the BP86 level of theory [28-30]. In all cases the electronic configuration of the molecular systems was described with the standard triple- ζ basis set augmented with one polarization functions of Ahlrichs and coworkers (TZVP keyword in Gaussian 03) for H, C, P, Si and Cl [31]. For Zr we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set (SDD keywords in Gaussian 03) [32]. Our choice of the above mentioned "functional" and "basis set" was based on several computational reports which suggest that these functional and basis set give very good results for a range of different transition metals containing catalytic systems, with a limited computational cost [33-36].

Characterization of the located stationary points as minima or transition state was performed by frequency calculations. The total energies and optimized

xyz coordinates are provided in the Supporting Information.

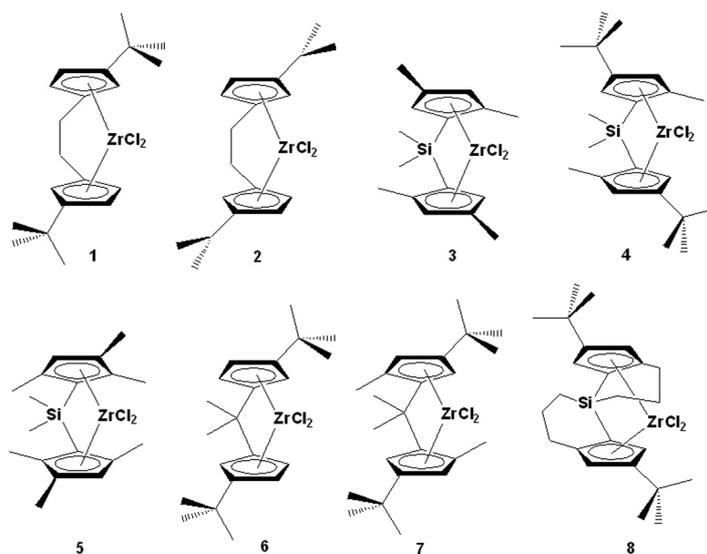
RESULTS AND DISCUSSION

The most successful and best studied *ansa*-metallocene catalysts for the stereoselective polymerization of propene are the chiral C_2 -symmetric zirconocenes, for

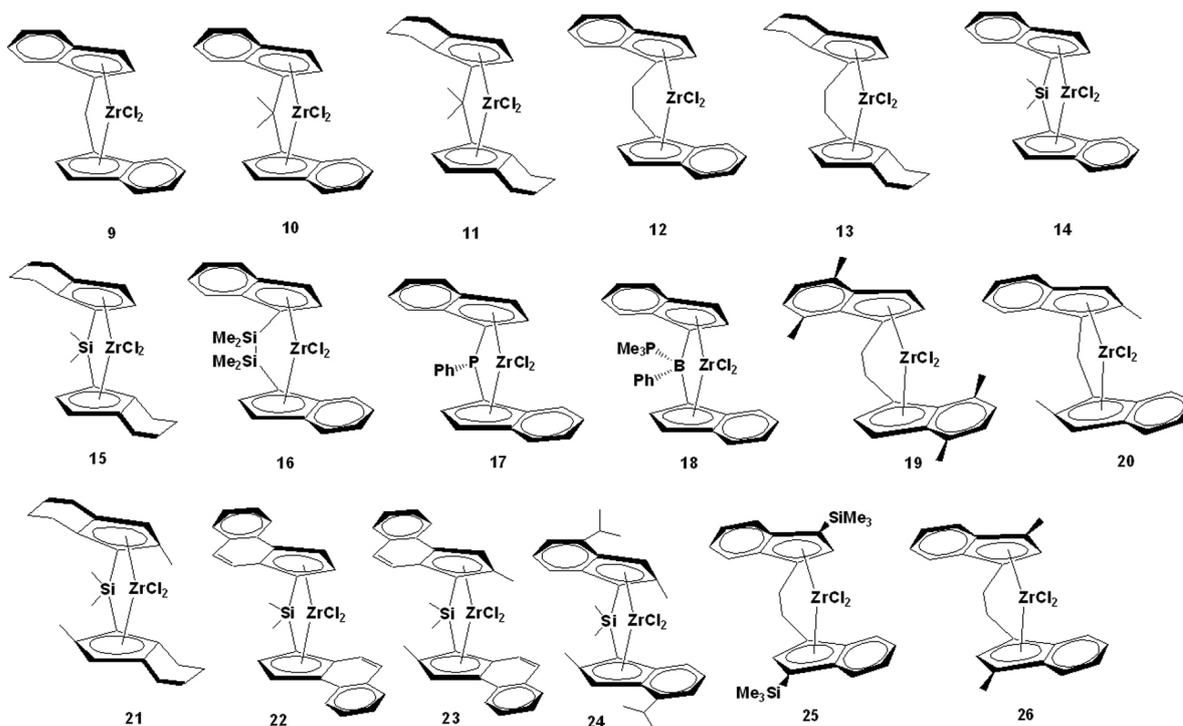
which a large number of insertion, isomerization, and chain release reactions have been documented [37]. These zirconium catalysts are isospecific, thanks to their symmetry, producing isotactic polypropenes. The 26 representative zirconocene systems analysed here are reported in Scheme 1.

In these systems, Zirconium bears two σ -ligands with chlorine atoms and two η^5 cyclopentadienyl ligands. The two cyclopentadienyl-type ligands are

Bis - Cp Zirconocene



Bis - Indenyl Zirconocene



Scheme 1. Most important zirconocene catalysts used in olefin polymerization

cyclopentadienyls itself ($C_5H_5^-$, Cp), alkylated cyclopentadienyls such as methyl, *tert*-butyl cyclopentadienyl and indenyls ($C_9H_7^-$, or Ind). The proper ligand symmetry in the systems analysed leads to all C_2 -symmetric complexes. Moreover, in all the systems two carbons of the polyhapto ligands are connected through a chemical bridge made by carbon, silicon, boron or phosphorus atoms depending on the system. The chemical bridge makes them stereorigid: they hold their C_2 -symmetry during the reaction steps, resulting in more or less selective systems towards isotactic polypropylene.

Since α -olefins are prochiral, in principle they can coordinate and insert into a metal-carbon bond in four different ways. Whether the olefin insertion is primary or secondary defines the regiochemistry of insertion; thus catalyst regioselectivity and the regioregularity of the polymer. In contrast, which enantioface of the olefin (*si* or *re*) coordinates to the metal (selected by the chain orientation) determines the stereochemistry of insertion; thus the catalyst stereoselectivity and the stereoregularity of the polymer.

As the insertion of an α -olefin into a metal-carbon bond is mostly primary (1,2), for the case of metallocenes, we focused only on this regiochemistry of insertion and we calculated the transition state energy for primary insertion of both the olefin enantiofaces. The theoretical stereoselectivity is computed as the energy difference between the two transition states described above, ΔE_{re-si} .

In Table 1 the DFT calculated energy differences between the *re* transition state and that of *si*, ΔE_{re-si} and the experimental values of the isotactic mmmm% pentad are reported.

Inspection of the data reported in Table 1 immediately shows a general correlation between the calculated ΔE_{re-si} and the experimental mmmm%. Although, our review article in Ref. [37] also summarizes similar comparison, here we try to develop a method to reliably predict the selectivity for metallocene catalysts not yet tested experimentally. To this end, a model was fitted to the experimentally obtained mmmm% against theoretical ΔE_{re-si} for primary insertion (Figure 1) and more systems were considered to achieve a more robust analysis. The data reported in Figure 1 graphically confirm that greater ΔE_{re-si} corresponds to the higher mmmm%. From a quantitative point of view, using a quadratic polynomial, the calculated ΔE_{re-si} correlate very well with the experimental stereoselectivity

Table 1. DFT calculated ΔE_{re-si} and the experimental values of the mmmm% pentad for the systems reported in Scheme 1.

Precatalyst	mmmm % ^[37]	ΔE_{re-si} (kcal·mol ⁻¹)
1	97.6	5.16
2	94.6	4.57
3	97.1	4.96
4	97.0	5.14
5	97.7	5.29
6	99.5	5.77
7	99.5	5.73
8	97.0	4.77
9	71.4	2.49
10	80.6	3.13
11	95.8	5.26
12	83.4	3.31
13	91.5	4.49
14	90.3	4.10
15	94.9	5.11
16	40.2	0.37
17	63.0	1.88
18	85.0	3.36
19	90.7	4.48
20	85.8	3.82
21	87.4	4.15
22	90.0	4.38
23	93.0	3.94
24	88.6	4.50
25	10.5	-0.76
26	19.9	-0.34

mmmm%, with a R^2 equal to 0.993. This value gives an indication of the accuracy that can be expected when DFT calculations are used to characterize the stereoselectivity (mmmm%) of new metallocene complexes for which the experimental data are not available. On the other hand, using a chemically more

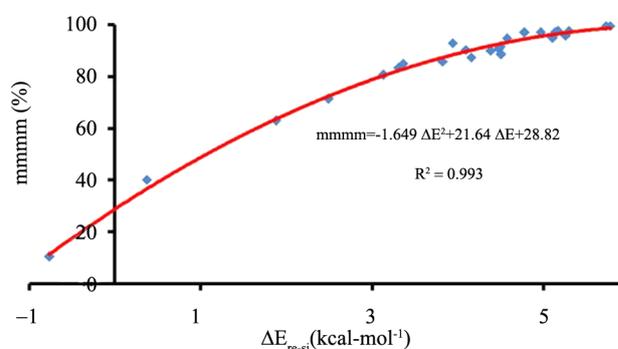


Figure 1. DFT calculated ΔE_{re-si} versus the experimental values of the pentad mmmm%. is from ^{13}C NMR. The values are referred to the total methyl signals. MMO as cocatalyst used in toluene.

sound expression of $p(\text{mmmm}) = \exp\left[\frac{-\Delta E_{\text{re-si}}}{kT}\right]^5$, where $p(\text{mmmm})$ is the probability of mmmm pentad, still a reasonable correlation, with a R^2 of 0.68, is achieved. However, since the scope here is to achieve the best possible correlation, we preferred to use and describe a quadratic polynomial.

To better rationalize as the steric hindrance of the ligands around the metal center affect the respective energies of the two diastereoisomeric transition states, a comparative analysis of the topographic steric

maps of two representative complexes, bis-Cp 1 and bis-Cp 2, is reported in Figure 2.

The points in space defining the steric maps were located with the SambVca package developed by Cavallo et al. [38] This program analyzes the first coordination sphere around the metal, which is the place where catalysis occurred. This is normally used to calculate the buried volume of a given ligand, which is a number that quantifies the amount of the first coordination sphere of the metal occupied by

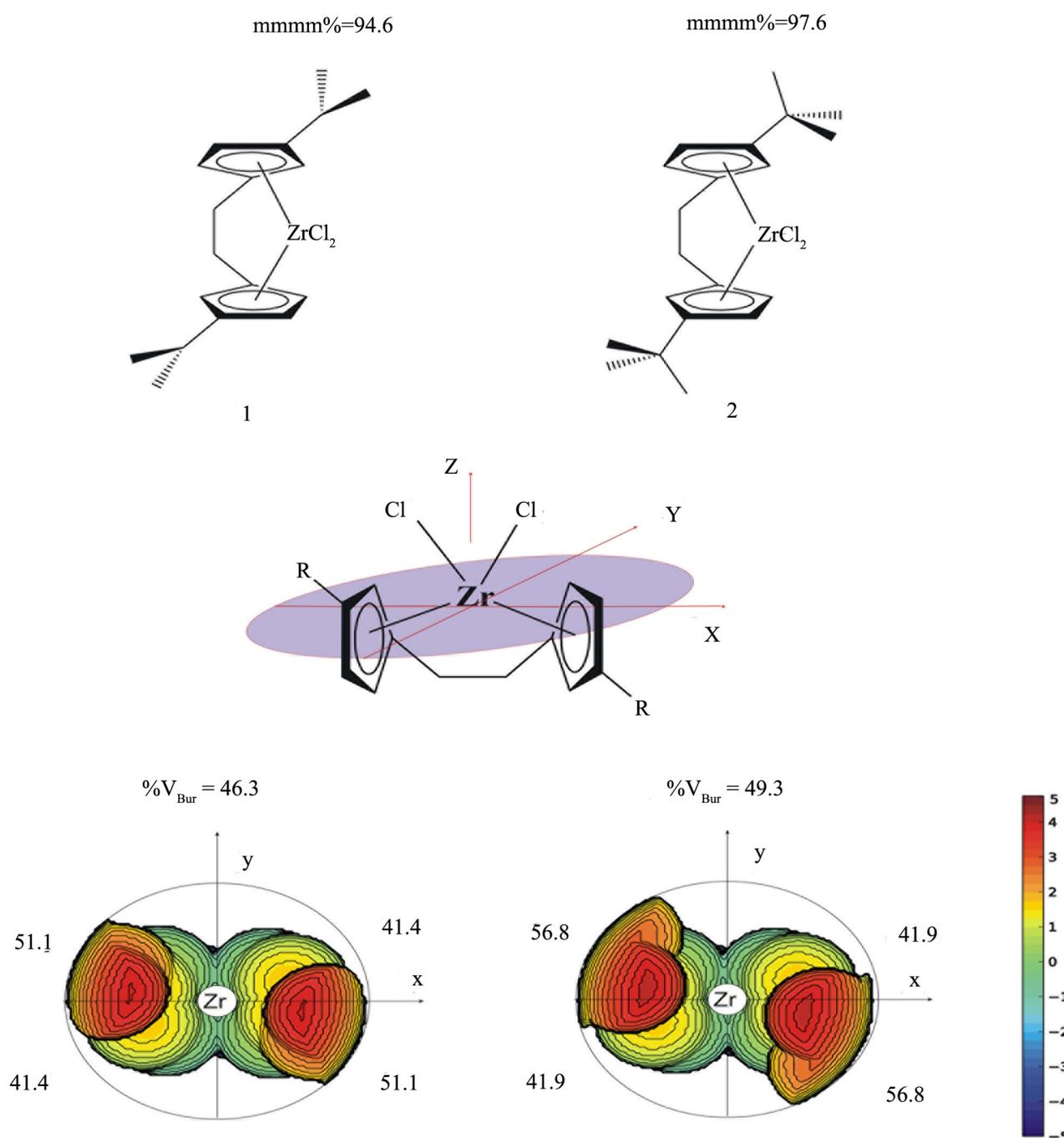


Figure 2. Topographic steric maps of bis-Cp 1 and bis-Cp 2 systems. The isocontour curves of the steric maps are in Å.

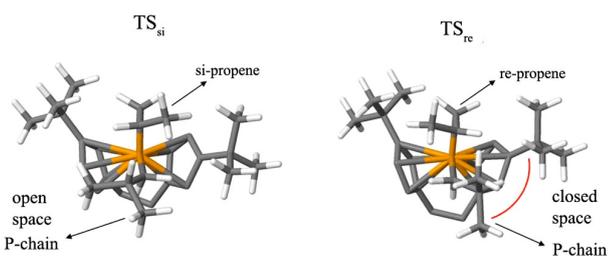


Figure 3. Geometry of the propene insertion transition states, TS_{si} and TS_{re} , for system bis-Cp₂

this ligand.[39-40] A modified version of SambVca allows the user to perform a more detailed analysis by evaluating the %V_{Bur} in single quadrants around the metal center. Splitting the total %V_{Bur} into quadrant contributions quantifies any asymmetry in the way the ligand wraps around the metal and allows one to understand how changing the ligand from iso-propyl to *tert*-butyl modifies the shape of the reactive pocket [39, 41-42] .

The steric contour maps reveal that, as expected, both systems 1 and 2 show an unsymmetrical distribution of the steric bulk of the Cp ligands around the metal, with the excess steric hindrance mainly localized around the substituent in position 3 on the rings (i.e., the quadrant up on the left and the quadrant down on the right).

Furthermore, the quadrants %V_{Bur} indicate that, moving from the *iso*-propyl group to the *tert*-butyl group, leads to a substantial increase of the localized steric hindrance. In each insertion step, due to the different position of the methyl group on the *si*-monomer with respect to that on the *re*-monomer, the bulky chain will be mainly localized into the more open quadrant in the TS_{si} and in the more close one in the TS_{re} (Figure 3).

Consequently, considered the higher steric hindrance of the *tert*-butyl substituents, the TS_{si} is energetically more favoured than the TS_{re} for the system 2 with respect to the system 1, making the former more stereoselective towards the *si* face of propene. This analysis is in agreement with the higher mmmm% of the polymer obtained with catalyst 2.

CONCLUSION

Metallocene systems have emerged as a successful class of catalyst for the polymerization of olefins. In particular, for propene-based polymers, metallocenes

have achieved a huge success thanks to the production of materials that cannot be made with heterogeneous catalysts.

In the last decade many efforts have been made to understand the details of the mechanisms of regio- and stereoselectivity. In fact, investigating and clarifying the key steps of the catalytic activity is the only way to improve the ligand design of the catalyst.

In this respect, the first part of this study is dedicated to an investigation of the performance of density functional theory method on the propene polymerization stereoselectivity of 26 zirconocene systems, using as benchmark the experimental results of the % of mmmm pentad present in the corresponding polymers.

The theoretical stereoselectivity is computed as the energy difference between the two transition states related to the *si*- and *re*-enantiofaces of the propylene coordination to the metal centre and named as ΔE_{re-si} . The obtained results showed that mmmm% increases as ΔE_{re-si} rises. In order to develop a method to predict, with highest reliability, the selectivity for metallocene catalysts, not yet tested experimentally, a model was fitted on the experimentally obtained mmmm% against theoretical ΔE_{re-si} . The use of DFT allowed the determination of the stereoregularity of metallocene catalysts using a simple ΔE_{re-si} determination. Given the importance to control the mmmm% of the polymers since it affects the chemical and physical properties of the resultant materials, having access to a such computational technique that could allow the improvement and/or the modulation of the catalysts performances through a rational catalyst design, may be an important goal to achieve. In the last part of this study, to better rationalize the effect of the steric hindrance of the ligands on the selectivity of metallocene catalysts, a comparative analysis of the topographic steric maps of two representative complexes *bis*-Cp 1 and *bis*-Cp 2 was considered. These maps give reason for the observation that catalysts with a greater %V_{Bur}, asymmetrically localized around the metal centre, lead to resultant polymers with a higher mmmm%.

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service (<http://www.molnac.unisa.it/OMtools/sambvca.php>) for computing $\%V_{\text{Bur}}$.

Supporting Information. Cartesian coordinates and energies in a.u. of all the species discussed in the text are available free of charge via the Internet at <http://poj.ippi.ac.ir/>.

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